

The Crystal Structure of Potassium Selenumtrithiocyanate Hemihydrate

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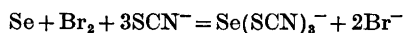
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Potassium selenumtrithiocyanate hemihydrate, $\text{KSe}(\text{SCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$, has been prepared from selenium oxidized by bromine and reacted with potassium thiocyanate.

The crystal structure has been determined by X-ray methods, and refined by full-matrix least squares procedures. The crystals are triclinic, space group $P\bar{1}$ (No. 2), with $a = 8.775(4) \text{ \AA}$, $b = 15.067(5) \text{ \AA}$, $c = 8.956(4) \text{ \AA}$, $\alpha = 119.64(3)^\circ$, $\beta = 101.03(3)^\circ$, $\gamma = 99.62(2)^\circ$, and four formula units per unit cell.

In the crystals, the selenumtrithiocyanate ions are dimerized. The two selenium atoms and the six sulfur atoms of the dimerized unit are approximately co-planar. The six cyano groups are located on the same side of the plane. Each of the two selenium atoms has an approximately square-planar coordination. The S—Se—S angles are in the range from $168.89(10)$ to $176.26(11)^\circ$ and from $84.24(8)$ to $98.52(12)^\circ$. There are four rather short Se—S bonds, from $2.252(2)$ to $2.318(3) \text{ \AA}$, and four long ones, from $2.906(3)$ to $3.112(3) \text{ \AA}$. The short ones are significantly longer than Se—S single-bond distance, 2.21 \AA , and the long ones are shorter than van der Waals approaches. Each long Se—S bond occurs *trans* to a short Se—S bond. The total lengths of the rather unsymmetrical approximately linear S—Se—S systems (the sums of the lengths of the two Se—S bonds) are from 5.197 to 5.364 \AA .

The salt, potassium selenumtrithionate hemihydrate, $\text{KSe}(\text{SCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$, has been isolated from an aqueous solution made by treating a suspension of selenium with bromine and then adding potassium thiocyanate. Without going into details concerning the reaction steps, the net reaction can be written:



The crystal structure of the analogous selenocyanate compound, potassium triselenocyanate hemihydrate, has been reported earlier.¹

EXPERIMENTAL

Preparation of potassium selenumtrithiocyanate hemihydrate. 0.05 mol (4 g) of selenium was suspended in 100 ml water of 50°C , and 0.046 mol (2.5 ml) of bromine was added under stirring. After the reaction was finished, a solution, heated to 50°C , of 0.25 mol (24 g) of KSCN in 50 ml water was added. The combined solution was filtered and then stored in a refrigerator for 5 h. The crystals which had deposited were filtered off and dried. Yield, 3.3 g, or 24 % based on the amount of bromine employed. (Found: Se 26.30 Calc. for $\text{KSe}(\text{SCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$: 26.24)

The salt can be recrystallized from a solution of 20 g KSCN in 50 ml water. The crystals are yellow triclinic prisms extended along the short *ac* diagonal.

CRYSTAL DATA

Collection of X-ray data was done by use of Nb-filtered $\text{MoK}\alpha$ radiation, $\lambda(\alpha_1) = 0.70926 \text{ \AA}$, by the same methods as for the analogous selenocyanate complex.¹ The cell parameters were evaluated from the θ angle of 11 resolved reflections.

$\text{KSe}(\text{SCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$, space group $P\bar{1}$ (No. 2), $a = 8.775(4) \text{ \AA}$, $b = 15.067(5) \text{ \AA}$, $c = 8.956(4) \text{ \AA}$, $\alpha = 119.64(3)^\circ$, $\beta = 101.09(3)^\circ$, $\gamma = 99.62(2)^\circ$, $Z = 4$. $D_x = D_m = 2.08 \text{ g/cm}^3$. Number of reflections recorded with measurable intensities, 2945 out of 5657 possible within $\theta = 30^\circ$. $\mu = 51.8 \text{ cm}^{-1}$.

The crystal used for data collection had the following dimensions, given as distances from the point of intersection of (111), (121), and (111); to (010), 0.034 mm; to (010), 0.052 mm; to (111), 0.10 mm; and to (111) 0.28 mm.

Intensities were corrected for absorption² and extinction.³

Table 1. Atomic coordinates for potassium selenumtrithiocyanate hemihydrate in fractions of triclinic cell edges. Origin at a centre of symmetry. Standard deviations from least squares are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Se ₁	0.22700(8)	0.11774(6)	-0.14168(10)
Se ₂	0.63014(7)	0.13601(6)	0.24619(10)
S ₁	0.2092(2)	0.1003(2)	-0.4130(3)
S ₂	-0.0257(2)	0.1268(2)	-0.1365(3)
S ₃	0.9017(2)	0.1552(2)	0.2830(3)
S ₄	0.6345(2)	0.1299(2)	0.5005(3)
S ₅	0.5981(2)	0.1456(2)	-0.0742(3)
S ₆	0.2890(2)	0.1247(2)	0.2005(3)
C ₁	0.2756(9)	0.2311(7)	-0.3350(10)
C ₂	0.0173(8)	0.2620(6)	-0.0099(10)
C ₃	0.9701(8)	0.2905(6)	0.4081(10)
C ₄	0.7362(9)	0.2597(7)	0.6513(10)
C ₅	0.6281(7)	0.2757(6)	0.0492(10)
C ₆	0.3474(8)	0.2574(6)	0.3104(10)
N ₁	0.3197(10)	0.3195(6)	-0.2840(10)
N ₂	0.0398(7)	0.3530(6)	0.0747(10)
N ₃	1.0188(7)	0.3827(6)	0.4949(10)
N ₄	0.8096(9)	0.3473(6)	0.7512(9)
N ₅	0.6495(8)	0.3669(6)	0.1389(10)
N ₆	0.3904(8)	0.3493(6)	0.3867(9)
O	0.4056(6)	0.4902(4)	0.1710(7)
K ₁	0.2654(2)	0.52154(14)	0.4509(2)
K ₂	0.8293(2)	0.52197(14)	0.1013(2)

Table 2. Anisotropic thermal parameters (Å²) in the form $\exp[-2\pi^2(h^2a^{-2}U_{11} + \dots + 2hka^{-1}b^{-1}U_{12} + \dots)]$. All values have been multiplied by 10³. Standard deviations from least squares refinement in parentheses.

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₂₃	<i>U</i> ₁₃
Se ₁	27.4(3)	17.1(3)	22.1(3)	6.9(2)	8.5(3)	5.4(2)
Se ₂	22.7(3)	13.9(3)	20.2(3)	4.4(2)	6.9(2)	3.1(2)
S ₁	50.5(9)	25.6(8)	21.5(8)	7.6(7)	9.1(7)	7.1(7)
S ₂	25.6(7)	23.5(8)	32.5(8)	4.3(6)	10.0(7)	6.1(6)
S ₃	26.6(7)	26.3(8)	36.6(9)	10.3(6)	14.3(7)	8.7(6)
S ₄	43.0(9)	28.6(9)	29.0(8)	5.7(7)	17.3(7)	6.0(7)
S ₅	37.1(8)	23.6(8)	30.2(8)	9.1(6)	10.2(7)	8.2(6)
S ₆	35.2(8)	27.5(8)	30.3(8)	4.4(6)	14.1(7)	7.2(6)
C ₁	48(4)	34(4)	24(3)	15(3)	17(3)	14(3)
C ₂	28(3)	28(3)	29(3)	9(3)	13(3)	6(2)
C ₃	27(3)	27(3)	34(3)	7(2)	17(3)	9(2)
C ₄	42(4)	29(3)	24(3)	11(3)	11(3)	9(3)
C ₅	23(3)	27(3)	32(3)	7(2)	16(3)	11(2)
C ₆	30(3)	28(3)	31(3)	12(3)	17(3)	14(2)
N ₁	93(5)	31(3)	38(4)	14(3)	19(3)	26(3)
N ₂	38(3)	32(3)	46(3)	12(3)	14(3)	11(3)
N ₃	37(3)	34(3)	51(4)	4(2)	23(3)	10(3)
N ₄	71(4)	42(4)	27(3)	15(3)	13(3)	11(3)
N ₅	51(3)	32(3)	45(4)	12(3)	18(3)	19(3)
N ₆	54(3)	34(3)	39(3)	17(3)	17(3)	18(3)
O	42(2)	36(3)	36(2)	12(2)	15(2)	13(2)
K ₁	37.3(7)	28.7(7)	33.4(8)	10.5(6)	14.3(6)	11.0(6)
K ₂	47.2(8)	30.2(8)	27.6(7)	6.8(6)	11.3(6)	12.9(6)

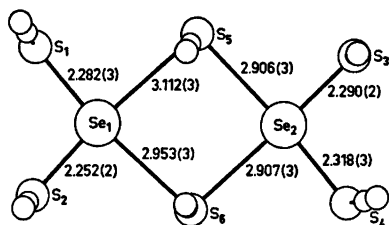


Fig. 1. The di- μ -thiocyanato-bis[dithiocyanato-selenate(II)] anion in $\text{KSe}(\text{SCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, as seen normal to the ac plane.

THE STRUCTURE ANALYSES

The structure was solved by Patterson and Fourier methods and by reference to the structure of $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$.

The R -value in the final full-matrix least squares refinement was 0.046. The Fourier difference map based on these data showed no higher peak than $0.3 \text{ e } \text{\AA}^3$.

Computational procedure and programs used are described elsewhere.³ The final atomic coordinates and temperature parameters are listed in Tables 1 and 2.

The structure factors are available from the author on request.

RESULTS

The di- μ -thiocyanato-bis[dithiocyanatoselenate(II)] anion. Bond lengths and angles in the anion, based on the atomic coordinates of

Table 1, are given in Fig. 1 and Table 3. Distances from the potassium ions and from the water molecule to neighbouring atoms are given in Table 4. The uncertainties in cell dimensions are taken into account in the given standard deviations.

As seen from Fig. 1, the seleniumtrithiocyanate ions are dimerized in the crystals. The two central atoms, Se_1 and Se_2 , the four terminal sulfur atoms, S_1 , S_2 , S_3 , and S_4 , and the two bridging sulfur atoms, S_5 and S_6 , are approximately co-planar. The largest deviation of an atom from a least squares plane is 0.21 \AA .

Each of the selenium atoms has a distorted square-planar environment, with long bonds to bridging sulfur atoms *trans* to rather short bonds to terminal sulfur atoms. The short bonds, from $2.252(2)$ to $2.318(3) \text{ \AA}$, are definitely longer than the Se-S single bond, 2.21 \AA . The long bonds are from $2.906(3)$ to $3.112(3) \text{ \AA}$, and thus shorter than van der Waals approaches. The S-Se-S angles of the four approximately linear S-Se-S systems are from $168.89(10)$ to $176.26(11)^\circ$.

The length of a symmetrical linear S-Se-S system (the sum of the lengths of the two Se-S bonds) is unknown. An estimated value can be derived from the length of the symmetrical linear Se-Se-Se system⁴⁻⁶ by subtracting the difference between the covalent radii of

Table 3. Angles ($^\circ$) in the dimerized seleniumtrithiocyanate ion and distances (\AA) in the thiocyanate groups in the same ion. Standard deviations in parentheses.

$\text{S}_1-\text{Se}_1-\text{S}_2$	98.52(12)	$\text{S}_3-\text{Se}_2-\text{S}_4$	95.50(11)
$\text{S}_2-\text{Se}_1-\text{S}_5$	89.38(11)	$\text{S}_4-\text{Se}_2-\text{S}_6$	86.50(10)
$\text{S}_5-\text{Se}_1-\text{S}_6$	84.24(8)	$\text{S}_5-\text{Se}_2-\text{S}_3$	88.87(9)
$\text{S}_6-\text{Se}_1-\text{S}_1$	88.48(10)	$\text{S}_6-\text{Se}_2-\text{S}_5$	89.09(10)
$\text{S}_1-\text{Se}_1-\text{S}_5$	171.38(10)	$\text{S}_3-\text{Se}_2-\text{S}_6$	176.26(11)
$\text{S}_2-\text{Se}_1-\text{S}_6$	168.89(10)	$\text{S}_4-\text{Se}_2-\text{S}_5$	175.31(9)
S_1-C_1	1.676(10)	$\angle \text{Se}_1-\text{S}_1-\text{C}_1$	97.9(3)
C_1-N_1	1.135(13)	$\angle \text{S}_1-\text{C}_1-\text{N}_1$	179.2(7)
S_2-C_2	1.695(8)	$\angle \text{Se}_1-\text{S}_2-\text{C}_2$	99.0(3)
C_2-N_2	1.148(11)	$\angle \text{S}_2-\text{C}_2-\text{N}_2$	177.2(5)
S_3-C_3	1.685(8)	$\angle \text{Se}_2-\text{S}_3-\text{C}_3$	97.5(3)
C_3-N_3	1.150(10)	$\angle \text{S}_3-\text{C}_3-\text{N}_3$	179.0(6)
S_4-C_4	1.669(7)	$\angle \text{Se}_2-\text{S}_4-\text{C}_4$	95.8(4)
C_4-N_4	1.132(10)	$\angle \text{S}_4-\text{C}_4-\text{N}_4$	177.5(7)
S_5-C_5	1.645(8)	$\angle \text{Se}_1-\text{S}_5-\text{C}_5$	86.9(2)
C_5-N_5	1.156(11)	$\angle \text{Se}_2-\text{S}_5-\text{C}_5$	90.4(4)
		$\angle \text{S}_5-\text{C}_5-\text{N}_5$	178.6(8)
S_6-C_6	1.658(9)	$\angle \text{Se}_1-\text{S}_6-\text{C}_6$	88.0(4)
C_6-N_6	1.147(11)	$\angle \text{Se}_2-\text{S}_6-\text{C}_6$	88.0(3)
		$\angle \text{S}_6-\text{C}_6-\text{N}_6$	178.9(6)

Table 4. Distances from the potassium ions and from the water molecule. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.^a

$K_1 \cdots N_2$	3.005(6)	$\angle N_2 \cdots K_1 \cdots N_6$	80.5(2)
$K_1 \cdots N_6^I$	2.827(9)	$\angle N_2 \cdots K_1 \cdots N_3^I$	74.2(3)
$K_1 \cdots N_3^I$	2.972(9)	$\angle N_6 \cdots K_1 \cdots N_3^I$	77.3(3)
$K_1 \cdots N_3^{II}$	3.089(8)	$\angle N_3^{II} \cdots K_1 \cdots N_6^{II}$	80.7(2)
$K_1 \cdots N_6^{II}$	3.050(8)	$\angle N_3^{II} \cdots K_1 \cdots N_3^{II}$	123.9(2)
$K_1 \cdots N_6^{II}$	2.931(6)	$\angle N_6^{II} \cdots K_1 \cdots N_6^{II}$	72.4(2)
$K_1 \cdots O$	2.868(7)		
$K_2 \cdots N_5$	2.792(10)	$\angle N_5 \cdots K_2 \cdots N_4^{III}$	86.6(3)
$K_2 \cdots N_4^{III}$	2.876(7)		
$K_2 \cdots N_1^{IV}$	2.847(9)	$\angle N_1^{IV} \cdots K_2 \cdots N_3^V$	73.7(2)
$K_2 \cdots N_3^V$	3.050(8)	$\angle N_1^{IV} \cdots K_2 \cdots N_4^V$	102.9(2)
$K_2 \cdots N_4^V$	3.069(7)	$\angle N_3^V \cdots K_2 \cdots N_4^V$	67.0(2)
$K_2 \cdots O^{IV}$	2.783(6)		
$O \cdots N_5$	3.028(10)	$\angle N_5 \cdots O \cdots N_1^{IV}$	87.9(3)
$O \cdots N_1^{IV}$	2.990(10)	$\angle N_5 \cdots O \cdots K_1$	113.9(3)
$O \cdots K_1$	2.868(7)	$\angle N_5 \cdots O \cdots K_2^{IV}$	129.7(2)
$O \cdots K_2^{IV}$	2.783(6)	$\angle N_1^{IV} \cdots O \cdots K_1$	113.2(2)
		$\angle N_1^{IV} \cdots O \cdots K_2^{IV}$	125.3(3)
		$\angle K_1 \cdots O \cdots K_2^{IV}$	106.9(2)

^a Superscript I denotes an atom at $(x-1, y, z)$, II at $(1-x, 1-y, 1-z)$, III at $(x, y, z-1)$, IV at $(1-x, 1-y, z)$, and V at $(2-x, 1-y, 1-z)$, where x, y, z are the coordinates of Table 1.

selenium and sulfur, $2(r_{Se}-r_S)$, which give $(5.31-0.26)$ Å = 5.05 Å. The total lengths of the unsymmetrical approximately linear S-Se-S systems in the present structure are from 5.197 to 5.364 Å, and thus 0.15 to 0.31 Å longer than the estimated value of a symmetrical linear S-Se-S arrangement.

The six cyano groups of the dimerized unit are all located on the same side of the least squares plane through the selenium atoms and the sulfur atoms. The Se-S-C angles are from 86.9(2) to 99.0(3)°. The S-C-N groups have only small, if any, significant deviation from linearity, the S-C-N angles

are from 177.2(5) to 179.2(7)°. The mean values of the S-C bond lengths and the C-N bond lengths are 1.671 and 1.145 Å, respectively, and there is no significant deviation from these mean values.

The present crystal structure shows great resemblance with the structures of the corresponding selenocyanate compounds^{1,7} with regard to the intra-ionic structure. But while the selenium atoms of the selenocyanate groups have a great tendency of forming interionic $Se \cdots Se$ contacts, to give double layers of selenium atoms, the sulfur atoms of the thiocyanate groups do not form such interionic

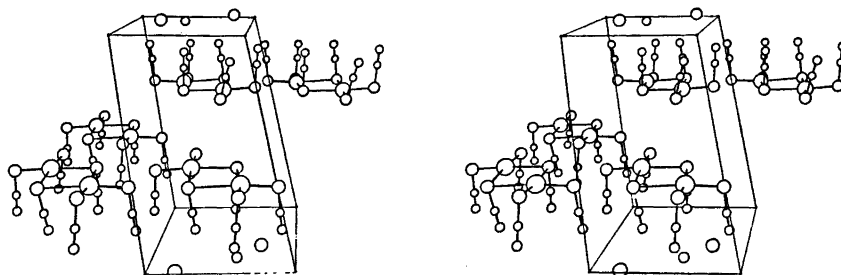


Fig. 2. A stereoscopic pair of drawings of $KSe(SCN)_3 \cdot \frac{1}{2}H_2O$. The cell drawn is along the a and c axis from 0 to 1 and along b axis from $-\frac{1}{2}$ to $\frac{1}{2}$.

S...Se or S...S contacts. The shortest inter-ionic S...Se distance in the present structure, between single layers, is 3.542(3) Å, and the shortest S...S distance is 3.486(3) Å.

In the crystal structure of $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}^1$ and the corresponding rubidium salt⁷ the dimerized seleniumtriselenocyanate ion can be looked upon as built up of two selenium diselenocyanate molecules, $\text{Se}(\text{SeCN})_2$, bridged together through the selenium atoms of two selenocyanate ions. In the present structure, the dimerized unit of seleniumtrithiocyanate can be looked upon as built up of two selenium dithiocyanate molecules, $\text{Se}(\text{SCN})_2$, bridged together through the sulfur atoms of two thiocyanate ions. In the crystals of selenium dithiocyanate,⁸ the molecules lie across a crystallographic mirror plane passing through the selenium atom, the Se-S bond lengths are 2.21 Å and the S-Se-S angle is 101°. Short Se-N contacts occur in directions which indicate a tendency to square-planar coordination at the selenium atom. The Se...N distances are 2.98 Å. In the present adduct with potassium thiocyanate, the selenium dithiocyanate molecules retain their approximate shape. The Se-S bond is now being approached at approximately 180° by a sulfur atom of a thiocyanate group instead of by the nitrogen end of a thiocyanate group. The approach is now stronger, resulting in a little longer Se-S bonds *trans* to the approach, and smaller S-Se-S angles. At Se_1 the sum of the two Se-S bond lengths is 4.534 Å and the angle is 98.52(12)°, and at Se_2 the sum is 4.608 Å and the angle is 95.50(11)°.

The environment of the potassium ions and the water molecule. The potassium ions and the water molecule lie at *y* approximately $\frac{1}{2}$, packed between nitrogen atoms with *y* about 0.35 and 0.65. The closest contacts of the potassium ions and the water molecule are listed in Table 4. The shapes of the resulting polyhedrons around the water molecule and the potassium ions are very much the same as found in the structure of $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}^1$.

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